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(54) MANUFACTURING METHOD FOR SILICATE FLUORESCENT MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a manufacturing method capable of obtaining a silicate fluorescent material having high brightness.

SOLUTION: A mixture comprising metal compounds and capable of being formed into the silicate fluorescent material by baking is manufactured by a sol-gel method and subsequently baked to manufacture the silicate fluorescent material. The silicate fluorescent material is constituted by adding at least one activator selected from the group consisting of Eu and Mn to a compound represented by the general formula: $mM1O.nM2O.2SiO_2$ (wherein, M1 is at least an element selected from the group consisting of Ca, Sr and Ba, M2 is at least one element selected from the group consisting of Mg and Zn, m is 0.5-3.5 and n is 0.5-2.5).

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(54) 【発明の名称】 ケイ酸塩蛍光体の製造方法

(57) 【要約】

【課題】輝度が高いケイ酸塩蛍光体を得られる製造方法を提供する。

【解決手段】金属化合物の混合物であって、焼成によりケイ酸塩蛍光体を構成しうる混合物をゾルゲル法により製造し、次いで焼成するケイ酸塩蛍光体の製造方法。ケイ酸塩蛍光体が一般式 $mM^1O \cdot nM^2O \cdot 2SiO_2$ (式中の M^1 は Ca、Sr および Ba からなる群より選ばれる1種以上、 M^2 は Mg および Zn からなる群より選ばれる1種以上、 m は 0.5 以上 3.5 以下、 n は 0.5 以上 2.5 以下である。) により表される化合物に、付活剤として Eu、Mn からなる群より選ばれる1種以上を含有してなるケイ酸塩蛍光体である上記製造方法。

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【特許請求の範囲】

【請求項1】金属化合物の混合物であって、焼成によりケイ酸塩蛍光体を構成しうる混合物をゾルゲル法により製造し、次いで焼成することを特徴とするケイ酸塩蛍光体の製造方法。

【請求項2】ケイ酸塩蛍光体が一般式 $mM^1O \cdot nM^2O \cdot 2SiO_2$ （式中の M^1 はCa、SrおよびBaからなる群より選ばれる1種以上、 M^2 はMgおよびZnからなる群より選ばれる1種以上、mは0.5以上3.5以下、nは0.5以上2.5以下である。）により表される化合物と、付活剤としてEu、Mnからなる群より選ばれる1種以上とを含有してなるケイ酸塩蛍光体である請求項1に記載のケイ酸塩蛍光体の製造方法。

【請求項3】ゾルゲル法による混合物の製造を、Ca、SrおよびBaからなる群より選ばれる1種以上の金属元素の塩またはアルコキシドと、MgおよびZnからなる群より選ばれる1種以上の金属元素の塩またはアルコキシドと、Siのアルコキシドと、EuおよびMnからなる群より選ばれる1種以上の金属元素の塩またはアルコキシドと溶媒とを混合し、加水分解を行い、溶媒を除去することにより行なう請求項2記載のケイ酸塩蛍光体の製造方法。

【請求項4】焼成における最高到達温度が800℃以上1400℃以下の温度範囲である請求項1～3のいずれかに記載の製造方法。

【請求項5】請求項1～4のいずれかに記載の製造方法によって得られたケイ酸塩蛍光体。

【請求項6】請求項5に記載の蛍光体を用いてなる真空紫外線励起発光素子。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、ケイ酸塩蛍光体の製造方法に関し、特にプラズマディスプレイパネル（PDP）、希ガスランプなどの真空紫外線励起発光素子用のケイ酸塩蛍光体の製造方法に関する。

【0002】

【従来の技術】ケイ酸塩蛍光体は、蛍光灯、ブラウン管、蓄光体、真空紫外線励起発光素子等に用いられている。ケイ酸塩蛍光体の製造方法としては、金属化合物の混合物であって、焼成によりケイ酸塩蛍光体を構成しうる混合物を焼成する製造方法が通常行われており、そして、前記金属化合物の混合物の製造方法は、原料となる金属化合物を該金属化合物の反応を伴うことなく混合して製造する方法が従来から行われてきた。

【0003】例えば、特開平11-246856号公報には、ケイ酸塩蛍光体の一つであり緑色蛍光体である $Zn_2SiO_4:Mn$ を、原料として酸化亜鉛（ ZnO ）、酸化ケイ素（ SiO_2 ）および酸化マンガン（ Mn_2O_3 ）を用い、それらの原料をボールミルで混合し、その後空气中で1200～1350℃の温度範囲で0.5

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時間焼成することにより製造する方法が開示されている。しかし、この方法により得られた蛍光体はその輝度が充分ではなく、さらに高い輝度を示すケイ酸塩蛍光体を得られる製造方法が求められていた。

【0004】

【発明が解決しようとする課題】本発明の目的は、輝度の高いケイ酸塩蛍光体およびその製造方法を提供することにある。

【0005】

【課題を解決するための手段】本発明者らは、ケイ酸塩蛍光体の製造方法について鋭意研究を重ねた結果、金属化合物の混合物であって焼成によりケイ酸塩蛍光体を構成しうる混合物として、ゾルゲル法により得られる混合物を用いると、発光輝度の高いケイ酸塩蛍光体が製造できることを見出し、本発明を完成するに至った。

【0006】すなわち本発明は、金属化合物の混合物であって、焼成によりケイ酸塩蛍光体を構成しうる混合物をゾルゲル法により製造し、次いで焼成するケイ酸塩蛍光体の製造方法を提供する。また本発明は、ケイ酸塩蛍光体が一般式 $mM^1O \cdot nM^2O \cdot 2SiO_2$ （式中の M^1 はCa、SrおよびBaからなる群より選ばれる1種以上、 M^2 はMgおよびZnからなる群より選ばれる1種以上、mは0.5以上3.5以下、nは0.5以上2.5以下である。）により表される化合物と、付活剤としてEu、Mnからなる群より選ばれる1種以上とを含有してなるケイ酸塩蛍光体である上記ケイ酸塩蛍光体の製造方法を提供する。また本発明は、ゾルゲル法による混合物の製造を、Ca、SrおよびBaからなる群より選ばれる1種以上の金属元素の塩またはアルコキシドと、MgおよびZnからなる群より選ばれる1種以上の金属元素の塩またはアルコキシドと、Siのアルコキシドと、EuおよびMnからなる群より選ばれる1種以上の金属元素の塩またはアルコキシドと溶媒とを混合し、加水分解を行い、溶媒を除去することにより行なう上記いずれかに記載のケイ酸塩蛍光体の製造方法を提供する。また本発明は、焼成における最高到達温度が800℃以上1400℃以下の温度範囲である上記いずれかに記載の製造方法を提供する。また本発明は、上記のいずれかに記載の製造方法によって得られたケイ酸塩蛍光体を提供する。さらに本発明は、前記ケイ酸塩蛍光体を用いてなる真空紫外線励起発光素子を提供する。

【0007】

【発明の実施の形態】以下に本発明について詳しく説明する。本発明のケイ酸塩蛍光体の製造方法は、金属化合物の混合物であって、焼成によりケイ酸塩蛍光体を構成しうる混合物を焼成するケイ酸塩蛍光体の製造方法に関し、その製造方法において、該金属化合物の混合物をゾルゲル法により製造することを特徴とする。本発明の製造方法においてゾルゲル法とは、金属化合物の微細な粒子が溶媒に分散した状態であるゾルの状態と、その微細

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な粒子が凝集して生成するゲルの状態とを経て金属化合物の混合物を得る混合物の製造方法であり、より具体的には、ケイ酸塩蛍光体を構成する金属元素と有機物の化合物（アルコキシド等の有機金属化合物）または金属元素の塩を溶媒に溶解し、次いで加水分解により該金属元素の化合物の微粒子を生成させ、溶媒の除去によって該金属元素の化合物の混合物を得る混合物の製造方法である。

【0008】金属アルコキシドを原料として用いる場合、アルコキシ基に関しては特に限定はなく、メトキシ基、エトキシ基、プロピオキシ基、ブトキシ基などが挙げられる。従って、例えばSiのアルコキシドとしては、テトラメトキシシラン（オルト珪酸メチル）、テトラエトキシシラン（オルト珪酸エチル）、テトラプロポキシシラン、テトラブトキシシラン等が挙げられる。また、金属塩を原料として用いる場合、塩の種類に関しては特に限定はなく、塩化物、硝酸塩、硫酸塩、酢酸塩、シュウ酸塩、塩化物、臭化物、フッ化物などが挙げられる。

【0009】次に、金属化合物の混合物を製造する方法について述べる。上記の金属アルコキシドまたは金属塩を有機溶媒に溶解し、金属溶液を作製する。有機溶媒としては、金属アルコキシドまたは金属塩を溶解できるものであればよく、例えば、メタノール、エタノール、n-プロピルアルコール、イソプロピルアルコール、ブタノール等のアルコール、エチレングリコール、エチレンオキシド、トリエタノールアミン等が挙げられる。

【0010】得られた上記の金属溶液と水を混合して加水分解を行い、ゾルを発生させる。加水分解速度を制御するために水を上記の有機溶媒で希釈しても良いし、加水分解後のゾルの粒子形状を制御するために、アンモニウム、エチレンジアミン、ピリジン等の塩基性触媒を添加しても良い。また金属溶液と水との混合時に攪拌しても良い。

【0011】得られたゾルの溶媒を除去して金属化合物の混合物を作製する。溶媒の除去方法は、特に限定されないが、ろ過、遠心沈降分離、エバポレーション、スプレードライ等を挙げることができる。また溶媒除去後、乾燥しても良い。乾燥温度は $-20 \sim 300^{\circ}\text{C}$ の範囲が好ましく、さらに好ましくは $90 \sim 200^{\circ}\text{C}$ である。

【0012】本発明の製造方法において、金属化合物の混合物を焼成する温度は、最高到達温度が 800°C から 1400°C の温度範囲が好ましい。焼成において、 800°C から 1400°C の温度範囲に保持する時間は $0.5 \sim 50$ 時間が好ましい。また、本焼成の前に、 600°C から 700°C の温度範囲にて仮焼することも可能である。焼成においては例えば、原料をアルミナボートに充填し、所定のガス雰囲気中で所定の温度で焼成することができる。また必要に応じて、原料に酸化ホウ素、フッ化アルミニウム等の反応促進剤（フラックス）を混合す

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ることにより、さらに結晶性が良好で輝度が高い本発明の蛍光体が得られることがある。

【0013】例えば、青色発光蛍光体である組成式 $\text{CaMgSi}_2\text{O}_6:\text{Eu}$ で表される化合物からなる蛍光体となるよう、ゾルゲル法で金属化合物の混合物を作製した場合、その金属化合物の混合物を焼成するときは、還元性雰囲気中で、 $800^{\circ}\text{C} \sim 1400^{\circ}\text{C}$ の温度範囲、 $0.5 \sim 40$ 時間の範囲で1回以上焼成するのが好ましい。還元性雰囲気を得る方法として、窒素と水素あるいは希ガスと水素の混合雰囲気中で焼成する方法等が挙げられる。また、これらの雰囲気に水蒸気が含まれていても良い。また、大気中で 800°C 以上 1400°C 以下の温度範囲で焼成した後、還元性雰囲気中で 800°C 以上 1400°C 以下の温度範囲で再度焼成することもできる。

【0014】上記方法にて得られる蛍光体を、ボールミルやジェットミル等を使用して粉碎することも、水等で洗浄することもでき、また必要に応じ分級することもできる。また、焼成を二度以上行うこともできる。焼成を繰り返すことにより、輝度がさらに高くなることがある。本発明によって得られるケイ酸塩蛍光体の粒子の内部の組成が均一となるためと思われ、理由は明らかではないが、本発明のケイ酸塩蛍光体は高い輝度を有しており、さらに色純度が良好なこともある。また、本発明によって得られるケイ酸塩蛍光体は一次粒子の凝集状態は、ゾルゲル法によらない従来の製造方法で得られたケイ酸塩蛍光体に比べて弱いものと思われ、粉碎が必要な場合であっても短時間で粉碎が行える。

【0015】本発明の製造方法において、ケイ酸塩蛍光体として、一般式 $\text{mM}^1\text{O} \cdot \text{nM}^2\text{O} \cdot 2\text{SiO}_2$ （式中の M^1 はCa、SrおよびBaからなる群より選ばれる1種以上、 M^2 はMgおよびZnからなる群より選ばれる1種以上、 m は 0.5 以上 3.5 以下、 n は 0.5 以上 2.5 以下である。）により表される化合物に、付活剤としてEu、Mnからなる群より選ばれる1種以上を含有してなるケイ酸塩蛍光体が好ましい。 m が 0.5 未満の場合、 m が 3.5 を超える場合、 n が 0.5 未満の場合、 n が 2.5 を超える場合のいずれかの場合においては、高い輝度を有するケイ酸塩蛍光体とはならないおそれがある。

【0016】本発明の製造方法において、ケイ酸塩蛍光体が前記ケイ酸塩蛍光体である場合、ゾルゲル法による混合物の製造を、Ca、SrおよびBaからなる群より選ばれる1種以上の金属元素の塩またはアルコキシドと、MgおよびZnからなる群より選ばれる1種以上の金属元素の塩またはアルコキシドと、Siのアルコキシドと、EuおよびMnからなる群より選ばれる1種以上の金属元素の塩またはアルコキシドと溶媒とを混合し、加水分解を行い、溶媒を除去することにより行なうことが好ましい。

【0017】例えば、青色発光蛍光体である CaMgS

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$\text{Si}_2\text{O}_6:\text{Eu}$ を製造するときは、焼成することにより $\text{CaMgSi}_2\text{O}_6:\text{Eu}$ を構成しうるCa、Ba、Mg、Euのアルコキンドまたは塩とSiのアルコキンドとを原料とすることができる。

【0018】本発明の製造方法により得られたケイ酸塩蛍光体は、輝度が高く、発光輝度の高いPDPなどの発光タイプの各種ディスプレイを作製することが可能となる。

【0019】本発明の真空紫外線励起発光表示素子用蛍光体を用いるPDPの作製方法としては、例えば、特開平10-195428号公報に開示されているような公知の方法が使用できる。すなわち、青色、緑色、赤色発光用のそれぞれの真空紫外線励起発光素子用蛍光体を、例えば、セルロース系化合物、ポリビニルアルコールのような高分子化合物および有機溶媒からなるバインダーと混合して蛍光物質ペーストを調製する。背面基板の内面の、隔壁で仕切られアドレス電極を備えたストライプ状の基板表面と隔壁面に、蛍光体ペーストをスクリーン印刷などの方法によって塗布し、300～600℃の温度範囲で焼成し、それぞれの蛍光体層を形成させる。これに、蛍光体層と直交する方向の透明電極およびバス電極を備え、内面に誘電体層と保護層を設けた表面ガラス基板を重ねて接着する。内部を排気して低圧のXeやNe等の希ガスを封入し、放電空間を形成させることにより、PDPを作製することができる。

【0020】本発明によって得られるケイ酸塩蛍光体は、真空紫外線励起下で高い輝度を得られるので、PDPや希ガスランプなどの真空紫外線励起発光素子に用いられるケイ酸塩蛍光体として極めて有用である。また本発明によるケイ酸塩蛍光体は、真空紫外線励起下のみならず、紫外線、陰極線あるいはX線励起下においても優れた発光特性を示す。

【0021】

【実施例】次に、本発明を実施例によりさらに詳しく説明するが、本発明はこれらの実施例に限定されるものではない。

【0022】実施例1

以下の原料が溶解したエタノール溶液（A液）を50ml調整した。

オルト珪酸エチル：0.1モル/L

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硝酸カルシウム2水和物：0.0485モル/L

硝酸マグネシウム6水和物：0.05モル/L

硝酸ユーロピウム6水和物：0.0015モル/L

また、以下の原料が溶解したエタノール溶液（B液）を50ml調整した。

アンモニア：2モル/L

水：3モル/L

次いでA液とB液を混合し、20時間攪拌してゾルを得た。またゾルの溶媒除去を遠心分離により行い、さらに50℃で真空乾燥を行い、金属化合物の混合物を得た。さらに得られた金属化合物の混合物をアルミナボートに充填し、2体積% H_2 含有Ar雰囲気中で1000℃の温度で2時間焼成して、組成式が $\text{Ca}_{0.97}\text{Eu}_{0.03}\text{MgSi}_2\text{O}_6$ で表される蛍光体を得た。この蛍光体に、6.7Pa（ 5×10^{-2} Torr）以下の真空槽内で、得られた蛍光体にエキシマ146nmランプ（ウシオ電機社製、H0012型）を用いて紫外線を照射したところ、青色に発光し、相対輝度は後述の比較例1を100とすると115であった。

【0023】比較例1

酸化ケイ素（ SiO_2 ）、炭酸カルシウム（ CaCO_3 ）、酸化ユーロピウム（ Eu_2O_3 ）、塩基性炭酸マグネシウム（ $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ ）各原料を $\text{CaCO}_3:\text{Eu}_2\text{O}_3:(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}:\text{SiO}_2$ のモル比が0.97:0.015:0.2:2になるように配合、混合した後、2体積% H_2 含有Ar雰囲気中で1000℃の温度で2時間焼成して、蛍光体を得た。この蛍光体に、6.7Pa（ 5×10^{-2} Torr）以下の真空槽内で、得られた蛍光体にエキシマ146nmランプ（ウシオ電機社製、H0012型）を用いて紫外線を照射したところ、青色に発光し、相対輝度は100であった。

【0024】

【発明の効果】本発明の製造方法によれば、発光輝度が高いケイ酸塩蛍光体を製造することができる。このケイ酸塩蛍光体は真空紫外線励起における発光輝度が高いので、プラズマディスプレイパネル（PDP）や希ガスランプなどの真空紫外線励起発光素子に好適な蛍光体として工業上極めて有用なものである。

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the silicate fluorescent substance which is the mixture of metallic compounds and is characterized by manufacturing the mixture which can constitute a silicate fluorescent substance by baking with a sol gel process, and subsequently calcinating it.

[Claim 2] a silicate fluorescent substance — general formula $mM1 O-nM2O$ and $2SiO_2$ ($M1$ in a formula — calcium —) 3.5 or less [0.5 or more] and n of one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which $M2$ becomes from Mg and Zn, and m are 2.5 or less [0.5 or more]. The manufacture approach of the silicate fluorescent substance according to claim 1 which is a silicate fluorescent substance which comes to contain one or more sorts chosen from the compound expressed and the group which consists of Eu and Mn as an activator.

[Claim 3] The salt or alkoxide of one or more sorts of metallic elements chosen from the group which consists of calcium, Sr, and Ba in manufacture of the mixture by the sol gel process, The salt or alkoxide of one or more sorts of metallic elements chosen from the group which consists of Mg and Zn, The manufacture approach of the silicate fluorescent substance according to claim 2 performed by hydrolyzing by mixing the alkoxide of Si, the salt of one or more sorts of metallic elements or alkoxide chosen from the group which consists of Eu and Mn, and a solvent, and removing a solvent.

[Claim 4] The manufacture approach according to claim 1 to 3 that the highest attainment temperature in baking is 800-degree-C or more temperature requirement 1400 degrees C or less.

[Claim 5] The silicate fluorescent substance obtained by the manufacture approach according to claim 1 to 4.

[Claim 6] The vacuum-ultraviolet-radiation excitation light emitting device which comes to use a fluorescent substance according to claim 5.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the silicate fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices, such as a plasma display panel (PDP) and a rare-gas lamp, especially about the manufacture approach of a silicate fluorescent substance.

[0002]

[Description of the Prior Art] The silicate fluorescent substance is used for a fluorescent lamp, the Braun tube, the luminous object, the vacuum-ultraviolet-radiation excitation light emitting device, etc. As the manufacture approach of a silicate fluorescent substance, it is the mixture of metallic compounds, and the manufacture approach of calcinating the mixture which can constitute a silicate fluorescent substance by baking is usually performed, and the method of mixing and manufacturing the metallic compounds with which the manufacture approach of the mixture of said metallic compounds serves as a raw material, without being accompanied by the reaction of these metallic compounds, has been performed from the former.

[0003] For example, the approach of manufacturing by mixing those raw materials with a ball mill, and calcinating after that $\text{Zn}_2\text{SiO}_4\text{:Mn}$ which is one of the silicate fluorescent substances, and is a green fluorescent substance in a 1200–1350-degree C temperature requirement in air for 0.5 hours, using a zinc oxide (ZnO), silicon oxide (SiO_2), and manganese oxide (Mn_2O_3) as a raw material, is indicated by JP,11-246856,A. However, that brightness of the fluorescent substance obtained by this approach was not enough, and the manufacture approach by which the silicate fluorescent substance in which still higher brightness is shown is obtained was searched for.

[0004]

[Problem(s) to be Solved by the Invention] The object of this invention is to offer the high silicate fluorescent substance and its manufacture approach of brightness.

[0005]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for the ability of a silicate fluorescent substance with high luminescence brightness to be manufactured, when the mixture obtained by the sol gel process was used as mixture which is the mixture of metallic compounds and can constitute a silicate fluorescent substance by baking as a result of repeating research wholeheartedly about the manufacture approach of a silicate fluorescent substance.

[0006] That is, this invention is the mixture of metallic compounds, manufactures the mixture which can constitute a silicate fluorescent substance by baking with a sol gel process, and offers the manufacture approach of the silicate fluorescent substance subsequently calcinated. moreover, this invention — a silicate fluorescent substance — general formula $m\text{M}_1\text{O}-n\text{M}_2\text{O}$ and 2SiO_2 (M_1 in a formula — calcium —) 3.5 or less [0.5 or more] and n of one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M_2 becomes from Mg and Zn, and m are 2.5 or less [0.5 or more]. The manufacture approach of the above-mentioned silicate fluorescent substance which is a silicate fluorescent substance which comes to contain one or more sorts chosen from the compound expressed and the group which consists of Eu and Mn as an activator is offered. Moreover, the salt or alkoxide of one or more sorts of metallic elements chosen from the group which this invention becomes from calcium, Sr, and Ba about manufacture of the mixture by the sol gel process, The salt or alkoxide of one or more sorts of metallic elements chosen from the group which consists of Mg and Zn, It hydrolyzes by mixing the alkoxide of Si, the salt of one or more sorts of metallic elements or alkoxide chosen from the group which consists of Eu and Mn, and a solvent, and one of the above performed by removing a solvent is provided with the manufacture approach of the silicate fluorescent substance a publication. Moreover, this invention provides with the manufacture approach of a publication one of the above whose highest attainment temperature in baking is 800-degree-C or more temperature requirements 1400 degrees C or less. Moreover, this invention offers the silicate fluorescent substance obtained by above either by the manufacture approach of a publication. Furthermore, this invention offers the vacuum-ultraviolet-radiation excitation light emitting device which comes to use said silicate fluorescent substance.

[0007]

[Embodiment of the Invention] This invention is explained in detail below. The manufacture approach of the silicate fluorescent substance of this invention is the mixture of metallic compounds, and is characterized by manufacturing the mixture of these metallic compounds with a sol gel process in the manufacture approach about the manufacture approach of a silicate fluorescent substance of calcinating the mixture which can constitute a silicate fluorescent substance by baking. The condition of the sol which is in the condition to which the detailed particle of metallic compounds distributed the sol gel process to the solvent in the manufacture approach of this invention, It is the manufacture approach of mixture of obtaining the mixture of metallic compounds through the condition of the gel which the detailed particle condenses and generates. More specifically The compound (organometallic compounds, such as an alkoxide) of the metallic element which constitutes a silicate fluorescent substance, and the organic substance, or the salt of a metallic element is dissolved in a solvent. Subsequently, it is the manufacture approach of mixture of making hydrolysis generating the particle of the compound of this metallic element, and obtaining the mixture of the compound of this metallic element by clearance of a solvent.

[0008] When using a metal alkoxide as a raw material, about an alkoxy group, there is especially no definition and a methoxy group, an ethoxy radical, a PUROI oxy-radical, a butoxy radical, etc. are mentioned. It follows, for example, a tetramethoxy silane (orthosilicic acid methyl), a tetra-ethoxy silane (ethyl orthosilicate), tetra-propoxysilane,

tetra-butoxysilane, etc. are mentioned as an alkoxide of Si. Moreover, when using a metal salt as a raw material, about the class of salt, there is especially no definition and a chloride, a nitrate, a sulfate, acetate, an oxalate, a chloride, a bromide, a fluoride, etc. are mentioned.

[0009] Next, how to manufacture the mixture of metallic compounds is described. An above-mentioned metal alkoxide or an above-mentioned metal salt is dissolved in an organic solvent, and a metal solution is produced. Alcohol, such as a methanol, ethanol, n-propyl alcohol, isopropyl alcohol, and a butanol, ethylene glycol, ethylene oxide, triethanolamine, etc. are mentioned that what is necessary is just what can dissolve a metal alkoxide or a metal salt as an organic solvent.

[0010] It hydrolyzes by mixing the above-mentioned metal solution and the water which were obtained, and a sol is generated. In order to dilute water with the above-mentioned organic solvent in order to control a hydrolysis rate, and to control the particle shape of the sol after hydrolysis, basic catalysts, such as ammonium, ethylenediamine, and a pyridine, may be added. Moreover, you may stir at the time of mixing with a metal solution and water.

[0011] The solvent of the obtained sol is removed and the mixture of metallic compounds is produced. Although especially the clearance approach of a solvent is not limited, it can mention filtration, centrifugation separation, evaporation, spray dry, etc. Moreover, you may dry after solvent clearance. The range of -20-300 degrees C is desirable still more desirable, and drying temperature is 90-200 degrees C.

[0012] In the manufacture approach of this invention, a 800 to 1400 degrees C temperature requirement has [the temperature which calcinates the mixture of metallic compounds] the desirable highest attainment temperature. In baking, the time amount held to a 800 to 1400 degrees C temperature requirement has 0.5 - 50 desirable hours. Moreover, it is also possible to carry out temporary quenching before this baking in a 600 to 700 degrees C temperature requirement. In baking, an alumina boat can be filled up with a raw material and it can be calcinated at predetermined temperature in a predetermined gas ambient atmosphere. Moreover, by mixing reaction accelerators (flux), such as boron oxide and aluminum fluoride, in a raw material, crystallinity is still better and the fluorescent substance of this invention with high brightness may be obtained if needed.

[0013] For example, when the mixture of metallic compounds is produced with a sol gel process and the mixture of the metallic compounds is calcinated so that it may become the fluorescent substance which consists of a compound expressed with empirical formula $\text{CaMgSi}_2\text{O}_6:\text{Eu}$ which is a blue luminescence fluorescent substance, it is desirable in a reducing atmosphere to calcinate once or more the temperature requirement of 800 degrees C - 1400 degrees C and in 0.5 - 40 hours. As an approach of acquiring a reducing atmosphere, the approach of calcinating in the mixed ambient atmosphere of nitrogen, hydrogen, or rare gas and hydrogen etc. is mentioned. Moreover, the steam may be contained in these ambient atmospheres. Moreover, after calcinating in atmospheric air in 800-degree-C or more temperature requirement 1400 degrees C or less, it can also calcinate again in a reducing atmosphere in 800-degree-C or more temperature requirement 1400 degrees C or less.

[0014] Grinding the fluorescent substance obtained by the above-mentioned approach using a ball mill, a jet mill, etc. can also be washed with water etc., and it can also be classified if needed. Moreover, it can also calcinate 2 times or more. By repeating baking, brightness may become still higher. Although it is considered because the presentation inside the particle of the silicate fluorescent substance obtained by this invention becomes uniform and a reason is not clear, the silicate fluorescent substance of this invention has high brightness, and has that color purity is also still better. Moreover, even if a weak potato is considered compared with the silicate fluorescent substance from which the state of aggregation of a primary particle was acquired by the conventional manufacture approach by the sol gel process and the silicate fluorescent substance obtained by this invention is a case to be ground, it can grind in a short time.

[0015] the manufacture approach of this invention — setting — as a silicate fluorescent substance — general formula $m\text{M}_1\text{O}-n\text{M}_2\text{O}$ and 2SiO_2 (M_1 in a formula — calcium —) 3.5 or less [0.5 or more] and n of one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M_2 becomes from Mg and Zn, and m are 2.5 or less [0.5 or more]. The silicate fluorescent substance which comes to contain one or more sorts chosen from the group which becomes the compound expressed from Eu and Mn as an activator is desirable. When m is less than 0.5, m exceeds 3.5 and n is less than 0.5, there is a possibility that it may not become the silicate fluorescent substance which has high brightness in one in case n exceeds 2.5 of cases.

[0016] The salt or alkoxide of one or more sorts of metallic elements chosen from the group which consists of calcium, Sr, and Ba in manufacture of the mixture by the sol gel process in the manufacture approach of this invention when a silicate fluorescent substance is said silicate fluorescent substance. The salt or alkoxide of one or more sorts of metallic elements chosen from the group which consists of Mg and Zn. It is desirable to carry out by hydrolyzing by mixing the alkoxide of Si, the salt of one or more sorts of metallic elements or alkoxide chosen from the group which consists of Eu and Mn, and a solvent, and removing a solvent.

[0017] For example, when manufacturing $\text{CaMgSi}_2\text{O}_6:\text{Eu}$ which is a blue luminescence fluorescent substance, the alkoxide of calcium, Ba, Mg, and Eu which can constitute $\text{CaMgSi}_2\text{O}_6:\text{Eu}$, or a salt and the alkoxide of Si can be used as a raw material by calcinating.

[0018] It becomes the silicate fluorescent substance obtained by the manufacture approach of this invention has high brightness, and possible to produce various displays luminescence type [, such as PDP with high luminescence brightness,].

[0019] As the production approach of PDP using the fluorescent substance for vacuum-ultraviolet-radiation excitation luminescence display devices of this invention, a well-known approach which is indicated by JP,10-195428,A can be used, for example. That is, blue, green, and each fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices for red luminescence are mixed with the binder which consists of for example, a cellulose type compound, a high molecular compound like polyvinyl alcohol, and an organic solvent, and a fluorescent material paste is prepared. A fluorescent substance paste is applied to stripe-like the substrate front face and septum side which were divided with the septum of the inner surface of a tooth-back substrate, and were equipped with the address electrode by approaches, such as screen-stencil, it calcinates to them in a 300-600-degree C temperature requirement, and each fluorescent substance layer is made to form in them. This is equipped with the transparent electrode and bus electrode of a direction which intersect perpendicularly with a fluorescent substance layer, and the surface glass substrate which prepared the dielectric layer and the protective layer in the inner surface is pasted up in piles. PDP is producible by exhausting the interior, enclosing rare gas, such as low-pressure Xe and Ne, and making discharge space form.

[0020] Since high brightness is obtained under vacuum-ultraviolet-radiation excitation, the silicate fluorescent substance obtained by this invention is very useful as a silicate fluorescent substance used for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp. Moreover, the silicate fluorescent substance by this invention shows the luminescence property which was excellent not only the bottom of vacuum-ultraviolet-radiation excitation but under ultraviolet rays, cathode rays, or X-ray excitation.

[0021]

[Example] Next, although an example explains this invention in more detail, this invention is not limited to these examples.

[0022] 50ml (A liquid) of ethanol solutions which the one or less-example raw material dissolved was adjusted.

ethyl-orthosilicate: — 0.1-mol / L calcium nitrate 2 hydrate: — 0.0485-mol / L magnesium nitrate 6 hydrate: — 0.05-mol / L nitric-acid europium 6 hydrate: — 0.0015mol/L — 50ml (B liquid) of ethanol solutions which the following raw materials dissolved was adjusted again.

ammonia: — two mols / L water: — 3mol/L — subsequently A liquid and B liquid were mixed, it stirred for 20 hours, and the sol was obtained. Moreover, centrifugal separation performed solvent clearance of a sol, the vacuum drying was performed at 50 more degrees C, and the mixture of metallic compounds was obtained. The alumina boat was filled up with the mixture of the metallic compounds furthermore obtained, it calcinated at the temperature of 1000 degrees C in the 2 volume %H₂ content Ar ambient atmosphere for 2 hours, and the empirical formula obtained the fluorescent substance expressed with calcium_{0.97}Eu_{0.03}MgSi₂O₆. When the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used at the fluorescent substance obtained within the vacuum tub below 6.7Pa (5x10⁻²Torr) and ultraviolet rays were irradiated, light was emitted blue at this fluorescent substance, and relative luminance was 115 when the below-mentioned example 1 of a comparison was set to 100.

[0023] Example of comparison 1 silicon oxide (SiO₂), a calcium carbonate (CaCO₃), Oxidation europium (Eu₂O₃) and basic-magnesium-carbonate (MgCO₃·4Mg(OH)·2.5H₂O) each raw material is blended so that the mole ratio of CaCO₃:Eu₂O₃:(MgCO₃)₄Mg(OH)₂·2.5H₂O:SiO₂ may be set to 0.97:0.015:0.2:2. After mixing, it calcinated at the temperature of 1000 degrees C in the 2 volume %H₂ content Ar ambient atmosphere for 2 hours, and the fluorescent substance was obtained. When the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used at the fluorescent substance obtained within the vacuum tub below 6.7Pa (5x10⁻²Torr) by this fluorescent substance and ultraviolet rays were irradiated, light was emitted blue and relative luminance was 100.

[0024]

[Effect of the Invention] According to the manufacture approach of this invention, a silicate fluorescent substance with high luminescence brightness can be manufactured. Since the luminescence brightness in vacuum-ultraviolet-radiation excitation is high, this silicate fluorescent substance is very useful on industry as a suitable fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices, such as a plasma display panel (PDP) and a rare-gas lamp.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the manufacture approach of the silicate fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices, such as a plasma display panel (PDP) and a rare-gas lamp, especially about the manufacture approach of a silicate fluorescent substance.

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PRIOR ART

[Description of the Prior Art] The silicate fluorescent substance is used for a fluorescent lamp, the Braun tube, the luminous object, the vacuum-ultraviolet-radiation excitation light emitting device, etc. As the manufacture approach of a silicate fluorescent substance, it is the mixture of metallic compounds, and the manufacture approach of calcinating the mixture which can constitute a silicate fluorescent substance by baking is usually performed, and the method of mixing and manufacturing the metallic compounds with which the manufacture approach of the mixture of said metallic compounds serves as a raw material, without being accompanied by the reaction of these metallic compounds, has been performed from the former.

[0003] For example, the approach of manufacturing by mixing those raw materials with a ball mill, and calcinating after that $\text{Zn}_2\text{SiO}_4\text{:Mn}$ which is one of the silicate fluorescent substances, and is a green fluorescent substance in a 1200-1350-degree C temperature requirement in air for 0.5 hours, using a zinc oxide (ZnO), silicon oxide (SiO_2), and manganese oxide (Mn_2O_3) as a raw material, is indicated by JP,11-246856,A. However, that brightness of the fluorescent substance obtained by this approach was not enough, and the manufacture approach by which the silicate fluorescent substance in which still higher brightness is shown is obtained was searched for.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to the manufacture approach of this invention, a silicate fluorescent substance with high luminescence brightness can be manufactured. Since the luminescence brightness in vacuum-ultraviolet-radiation excitation is high, this silicate fluorescent substance is very useful on industry as a suitable fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices, such as a plasma display panel (PDP) and a rare-gas lamp.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The object of this invention is to offer the high silicate fluorescent substance and its manufacture approach of brightness.

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MEANS

[Means for Solving the Problem] this invention persons came to complete a header and this invention for the ability of a silicate fluorescent substance with high luminescence brightness to be manufactured, when the mixture obtained by the sol gel process was used as mixture which is the mixture of metallic compounds and can constitute a silicate fluorescent substance by baking as a result of repeating research wholeheartedly about the manufacture approach of a silicate fluorescent substance.

[0006] That is, this invention is the mixture of metallic compounds, manufactures the mixture which can constitute a silicate fluorescent substance by baking with a sol gel process, and offers the manufacture approach of the silicate fluorescent substance subsequently calcinated. moreover, this invention — a silicate fluorescent substance — general formula $mM1 O-nM2O$ and $2SiO_2$ ($M1$ in a formula — calcium —) 3.5 or less [0.5 or more] and n of one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which $M2$ becomes from Mg and Zn, and m are 2.5 or less [0.5 or more]. The manufacture approach of the above-mentioned silicate fluorescent substance which is a silicate fluorescent substance which comes to contain one or more sorts chosen from the compound expressed and the group which consists of Eu and Mn as an activator is offered. Moreover, the salt or alkoxide of one or more sorts of metallic elements chosen from the group which this invention becomes from calcium, Sr, and Ba about manufacture of the mixture by the sol gel process. The salt or alkoxide of one or more sorts of metallic elements chosen from the group which consists of Mg and Zn. It hydrolyzes by mixing the alkoxide of Si, the salt of one or more sorts of metallic elements or alkoxide chosen from the group which consists of Eu and Mn, and a solvent, and one of the above performed by removing a solvent is provided with the manufacture approach of the silicate fluorescent substance a publication. Moreover, this invention provides with the manufacture approach of a publication one of the above whose highest attainment temperature in baking is 800-degree-C or more temperature requirements 1400 degrees C or less. Moreover, this invention offers the silicate fluorescent substance obtained by above either by the manufacture approach of a publication. Furthermore, this invention offers the vacuum-ultraviolet-radiation excitation light emitting device which comes to use said silicate fluorescent substance.

[0007] [Embodiment of the Invention] This invention is explained in detail below. The manufacture approach of the silicate fluorescent substance of this invention is the mixture of metallic compounds, and is characterized by manufacturing the mixture of these metallic compounds with a sol gel process in the manufacture approach about the manufacture approach of a silicate fluorescent substance of calcinating the mixture which can constitute a silicate fluorescent substance by baking. The condition of the sol which is in the condition to which the detailed particle of metallic compounds distributed the sol gel process to the solvent in the manufacture approach of this invention. It is the manufacture approach of mixture of obtaining the mixture of metallic compounds through the condition of the gel which the detailed particle condenses and generates. More specifically The compound (organometallic compounds, such as an alkoxide) of the metallic element which constitutes a silicate fluorescent substance, and the organic substance, or the salt of a metallic element is dissolved in a solvent. Subsequently, it is the manufacture approach of mixture of making hydrolysis generating the particle of the compound of this metallic element, and obtaining the mixture of the compound of this metallic element by clearance of a solvent.

[0008] When using a metal alkoxide as a raw material, about an alkoxy group, there is especially no definition and a methoxy group, an ethoxy radical, a PUROI oxy-radical, a butoxy radical, etc. are mentioned. It follows, for example, a tetramethoxy silane (orthosilicic acid methyl), a tetra-ethoxy silane (ethyl orthosilicate), tetra-propoxysilane, tetra-butoxysilane, etc. are mentioned as an alkoxide of Si. Moreover, when using a metal salt as a raw material, about the class of salt, there is especially no definition and a chloride, a nitrate, a sulfate, acetate, an oxalate, a chloride, a bromide, a fluoride, etc. are mentioned.

[0009] Next, how to manufacture the mixture of metallic compounds is described. An above-mentioned metal alkoxide or an above-mentioned metal salt is dissolved in an organic solvent, and a metal solution is produced. Alcohol, such as a methanol, ethanol, n-propyl alcohol, isopropyl alcohol, and a butanol, ethylene glycol, ethylene oxide, triethanolamine, etc. are mentioned that what is necessary is just what can dissolve a metal alkoxide or a metal salt as an organic solvent.

[0010] It hydrolyzes by mixing the above-mentioned metal solution and the water which were obtained, and a sol is generated. In order to dilute water with the above-mentioned organic solvent in order to control a hydrolysis rate, and to control the particle shape of the sol after hydrolysis, basic catalysts, such as ammonium, ethylenediamine, and a pyridine, may be added. Moreover, you may stir at the time of mixing with a metal solution and water.

[0011] The solvent of the obtained sol is removed and the mixture of metallic compounds is produced. Although especially the clearance approach of a solvent is not limited, it can mention filtration, centrifugation separation, evaporation, spray dry, etc. Moreover, you may dry after solvent clearance. The range of -20-300 degrees C is desirable still more desirable, and drying temperature is 90-200 degrees C.

[0012] In the manufacture approach of this invention, a 800 to 1400 degrees C temperature requirement has [the temperature which calcinates the mixture of metallic compounds] the desirable highest attainment temperature. In baking, the time amount held to a 800 to 1400 degrees C temperature requirement has 0.5 - 50 desirable hours. Moreover, it is also possible to carry out temporary quenching before this baking in a 600 to 700 degrees C temperature requirement. In baking, an alumina boat can be filled up with a raw material and it can be calcinated at predetermined temperature in a predetermined gas ambient atmosphere. Moreover, by mixing reaction accelerators (flux), such as boron oxide and aluminum fluoride, in a raw material, crystallinity is still better and the fluorescent

substance of this invention with high brightness may be obtained if needed.

[0013] For example, when the mixture of metallic compounds is produced with a sol gel process and the mixture of the metallic compounds is calcinated so that it may become the fluorescent substance which consists of a compound expressed with empirical formula $\text{CaMgSi}_2\text{O}_6\text{:Eu}$ which is a blue luminescence fluorescent substance, it is desirable in a reducing atmosphere to calcinate once or more the temperature requirement of 800 degrees C – 1400 degrees C and in 0.5 – 40 hours. As an approach of acquiring a reducing atmosphere, the approach of calcinating in the mixed ambient atmosphere of nitrogen, hydrogen, or rare gas and hydrogen etc. is mentioned. Moreover, the steam may be contained in these ambient atmospheres. Moreover, after calcinating in atmospheric air in 800-degree-C or more temperature requirement 1400 degrees C or less, it can also calcinate again in a reducing atmosphere in 800-degree-C or more temperature requirement 1400 degrees C or less.

[0014] Grinding the fluorescent substance obtained by the above-mentioned approach using a ball mill, a jet mill, etc. can also be washed with water etc., and it can also be classified if needed. Moreover, it can also calcinate 2 times or more. By repeating baking, brightness may become still higher. Although it is considered because the presentation inside the particle of the silicate fluorescent substance obtained by this invention becomes uniform and a reason is not clear, the silicate fluorescent substance of this invention has high brightness, and has that color purity is also still better. Moreover, even if a weak potato is considered compared with the silicate fluorescent substance from which the state of aggregation of a primary particle was acquired by the conventional manufacture approach by the sol gel process and the silicate fluorescent substance obtained by this invention is a case to be ground, it can grind in a short time.

[0015] the manufacture approach of this invention — setting — as a silicate fluorescent substance — general formula $m\text{M1 O-nM2O and } 2\text{SiO}_2$ (M1 in a formula — calcium —) 3.5 or less [0.5 or more] and n of one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M2 becomes from Mg and Zn, and m are 2.5 or less [0.5 or more]. The silicate fluorescent substance which comes to contain one or more sorts chosen from the group which becomes the compound expressed from Eu and Mn as an activator is desirable. When m is less than 0.5, m exceeds 3.5 and n is less than 0.5, there is a possibility that it may not become the silicate fluorescent substance which has high brightness in one in case n exceeds 2.5 of cases.

[0016] The salt or alkoxide of one or more sorts of metallic elements chosen from the group which consists of calcium, Sr, and Ba in manufacture of the mixture by the sol gel process in the manufacture approach of this invention when a silicate fluorescent substance is said silicate fluorescent substance, The salt or alkoxide of one or more sorts of metallic elements chosen from the group which consists of Mg and Zn, It is desirable to carry out by hydrolyzing by mixing the alkoxide of Si, the salt of one or more sorts of metallic elements or alkoxide chosen from the group which consists of Eu and Mn, and a solvent, and removing a solvent.

[0017] For example, when manufacturing $\text{CaMgSi}_2\text{O}_6\text{:Eu}$ which is a blue luminescence fluorescent substance, the alkoxide of calcium, Ba, Mg, and Eu which can constitute $\text{CaMgSi}_2\text{O}_6\text{:Eu}$, or a salt and the alkoxide of Si can be used as a raw material by calcinating.

[0018] It becomes the silicate fluorescent substance obtained by the manufacture approach of this invention has high brightness, and possible to produce various displays luminescence type [, such as PDP with high luminescence brightness,].

[0019] As the production approach of PDP using the fluorescent substance for vacuum-ultraviolet-radiation excitation luminescence display-devices of this invention, a well-known approach which is indicated by JP,10-195428,A can be used, for example. That is, blue, green, and each fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices for red luminescence are mixed with the binder which consists of for example, a cellulose type compound, a high molecular compound like polyvinyl alcohol, and an organic solvent, and a fluorescent material paste is prepared. A fluorescent substance paste is applied to stripe-like the substrate front face and septum side which were divided with the septum of the inner surface of a tooth-back substrate, and were equipped with the address electrode by approaches, such as screen-stencil, it calcinates to them in a 300-600-degree C temperature requirement, and each fluorescent substance layer is made to form in them. This is equipped with the transparent electrode and bus electrode of a direction which intersect perpendicularly with a fluorescent substance layer, and the surface glass substrate which prepared the dielectric layer and the protective layer in the inner surface is pasted up in piles. PDP is producible by exhausting the interior, enclosing rare gas, such as low-pressure Xe and Ne, and making discharge space form.

[0020] Since high brightness is obtained under vacuum-ultraviolet-radiation excitation, the silicate fluorescent substance obtained by this invention is very useful as a silicate fluorescent substance used for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp. Moreover, the silicate fluorescent substance by this invention shows the luminescence property which was excellent not only the bottom of vacuum-ultraviolet-radiation excitation but under ultraviolet rays, cathode rays, or X-ray excitation.

[Translation done.]

* NOTICES *

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- 3.In the drawings, any words are not translated.

- EXAMPLE

[Example] Next, although an example explains this invention in more detail, this invention is not limited to these examples.

[0022] 50ml (A liquid) of ethanol solutions which the one or less-example raw material dissolved was adjusted. ethyl-orthosilicate: — 0.1-mol / L calcium nitrate 2 hydrate: — 0.0485-mol / L magnesium nitrate 6 hydrate: — 0.05-mol / L nitric-acid europium 6 hydrate: — 0.0015mol/L — 50ml (B liquid) of ethanol solutions which the following raw materials dissolved was adjusted again.

ammonia: — two mols / L water: — 3mol/L — subsequently A liquid and B liquid were mixed, it stirred for 20 hours, and the sol was obtained. Moreover, centrifugal separation performed solvent clearance of a sol, the vacuum drying was performed at 50 more degrees C, and the mixture of metallic compounds was obtained. The alumina boat was filled up with the mixture of the metallic compounds furthermore obtained, it calcinated at the temperature of 1000 degrees C in the 2 volume %H₂ content Ar ambient atmosphere for 2 hours, and the empirical formula obtained the fluorescent substance expressed with calcium_{0.97}Eu_{0.03}MgSi₂O₆. When the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used at the fluorescent substance obtained within the vacuum tub below 6.7Pa (5x10⁻²Torr) and ultraviolet rays were irradiated, light was emitted blue at this fluorescent substance, and relative luminance was 115 when the below-mentioned example 1 of a comparison was set to 100.

[0023] Example of comparison 1 silicon oxide (SiO₂), a calcium carbonate (CaCO₃), Oxidation europium (Eu₂O₃) and basic-magnesium-carbonate (MgCO₃) (4Mg (OH) 2.5H₂O) each raw material is blended so that the mole ratio of CaCO₃:Eu₂O₃:(MgCO₃)4Mg(OH)2.5H₂O:SiO₂ may be set to 0.97:0.015:0.2:2. After mixing, it calcinated at the temperature of 1000 degrees C in the 2 volume %H₂ content Ar ambient atmosphere for 2 hours, and the fluorescent substance was obtained. When the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used at the fluorescent substance obtained within the vacuum tub below 6.7Pa (5x10⁻²Torr) by this fluorescent substance and ultraviolet rays were irradiated, light was emitted blue and relative luminance was 100.

[Translation done.]